Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 16 (2015) 723 – 727

Procedia Chemistry

International Symposium on Applied Chemistry 2015 (ISAC 2015)

Effect of Regeneration Temperature onParticle Characteristics and Extent of Regeneration of Saturated SO_2-Adsorption ofCuO/γ-Al_2O_3 Adsorbent

David Bahrin[a], Subagjo[a], Herri Susanto[a,]*

[a]Department of Chemical Engineering InstitutTeknologi Bandung, Bandung 40132 Indonesia

Abstract

The effect of regeneration temperature on characteristics and extent of desorption of saturatedCuO/γ-Al_2O_3 have been studied. Adsorbent CuO/γ-Al_2O_3(8%-Cu) was prepared using the dry impregnation method with $Cu(NO_3)_2.3H_2O$ solution on a commercial γ-Al_2O_3. SO_2 adsorption process of the adsorbent CuO/γ-Al_2O_3were conducted on temperature of 400°C with a concentration of SO_2 in a model gas of 18500 ppmv and the initial weight of adsorbent of 1.0 gram. Regeneration of saturated adsorbent were carried out under air flowat various temperatures of 500, 600 or 700°C. Both of adsorption and regeneration experiments were carried out with a flowrateof model gas or air of 1.4 – 1.8 mL/sec for 60 minutes.Extent of desorption of saturated adsorbent CuO/γ-Al_2O_3were measured based on the different weight of the adsorbent between the beginning and the end of adsorption and regeneration process. Regeneration temperaturesof 500 and 600°C did not significantly effect the averagepore diameter of adsorbent.But that of 700°Caffectedthe specific surface area and averagepore diameter ofthe adsorbentsignificantly. The extent of desorption of the saturated adsorbentCuO/γ-Al_2O_3at the regeneration temperature of 600°Cwas higher thanthose of 500and700°C. Up to four adsorption-desorptioncycles, the extent of desorption were more less constant.This experimental results reveal a promising method for the development of flue gas desulfurization related the use of coal with a high sulfur content in power stations.

Peer-review under responsibility of Research Center for Chemistry, Indonesian Institute of Sciences

* Corresponding author. Tel.: +62 222 511 067; fax: +62 222 530 689.
*E-mail address:*herri@che.itb.ac.id

Peer-review under responsibility of Research Center for Chemistry, Indonesian Institute of Sciences
doi:10.1016/j.proche.2015.12.020

Keywords: characteristics; $CuO/\gamma\text{-}Al_2O_3$; pore properties; SO_2 release

Nomenclature

BET	brunauer, emmett, teller	**Å**	angstroms, unit of pore diameter	**cm**	centimeter
ppmv	parts per millionbyvolume	**°C**	degree of celcius	**m**	meter
mL	miliLiter	**gr**	gram	**sec**	second

1. Introduction

Consumption of coal for power plant in Indonesia is estimatedto be about 250 million tonnes/year in 2030[1]. As there is a tendency to use the available low quality coal, emission of harmful SO_2 will also increase.This lead to the development of an effective and economically attractive method for reduction of SO_2 emission.The conventional flue gas desulfurization using limestone or lime is able to capture SO_2 effectively, but this technology produces $CaCO_3$ as solid waste. Adsorbent $CuO/\gamma\text{-}Al_2O_3$has been considered as a promising catalyst for SO_2 removal from the flue gas[2,3,4,5]. Together with SO_2, NO_x may also been adsorption too. Saturated adsorbent ($CaSO_4$) can be regenerated and used for the next adsorption cycle. This adsorbent may be used up to several adsorption-desorption cycles without any significant decrease in its capacity, no-changein physical and chemical properties [3,5,6].

Regeneration of the adsorbent $CuO/\gamma\text{-}Al_2O_3$ can be conductedunder a reductive gases, such as H_2, CO, CH_4 or NH_3 and/or using the thermal decomposition[3].During the desorption process, SO_3 (instead of SO_2) leaves the adsorbent. This gaseous product, SO_3can then be converted into sulphuric acid. This adsorption-desorption of SO_2 on a Cu-based adsorbent has an advantage against the conventional Claus with respect to SO_2 content in the flue gas.

Desorption of $SO_3$from $CuSO_4$can be carried out using the thermal decomposition underthe flowing hot inert gas, or air[3].The decomposition temperature of $CuSO_4$ is 600°C, and that of $Al_2(SO_4)_3$ is above 700°C in N_2atmosphere[7].Reactions of the adsorption of $SO_2$and subsequent regeneration of the saturated adsorbent or desorption of SO_3 may represented as follows [7].

$$CuO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CuSO_{4(s)} \quad (1)$$

$$CuSO_{4(s)} \leftrightarrow CuO_{(s)} + SO_{3(g)} \quad (2)$$

$$Al_2O_{3(s)} + 3SO_{3(g)} \rightarrow Al_2(SO_4)_{3(s)} \quad (3)$$

Reaction (1) and reaction (3) readily occurs at 300°C or above[2,3]. Reactions (2) may take place at above 450°C[9].Care must be taken that reaction (3) or formation of $Al_2(SO_4)_3$must be avoided, since its regeneration is very difficult.

Our previous experiments indicated that the regeneration of the saturated adsorbent could be conducted in under flowing air at a temperature of 600°C for 20 minutes[1]. Furthermore, we found that the adsorbent could be used repeatedly up to four times in adsorption-desorption mode without significant decrease in its activity.In this paper we report our study focused on the effect of temperature regeneration on the characteristics of the adsorbent $CuO/\gamma\text{-}Al_2O_3$ as a solid particle.

2. Methodology

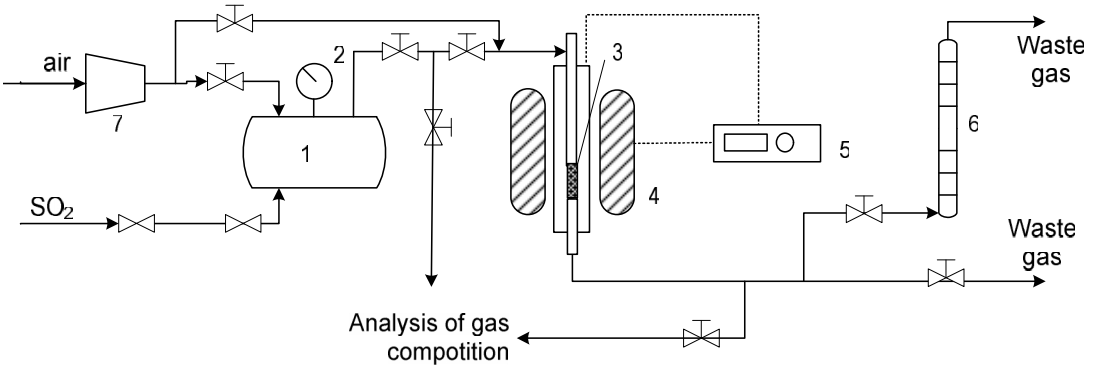
2.1 Preparation and Characterization ofAdsorbent $CuO/\gamma\text{-}Al_2O_3$

Adsorbent $CuO/\gamma\text{-}Al_2O_3$was synthesized through the dry impregnation of a commercial $\gamma\text{-}Al_2O_3$support. Solution of $Cu(NO_3)_2.3H_2O$was used as a source of the active phase (Cu). The impregnated support was then dried in two steps: at a temperature of 50°C for 8 hour and at 120°C for 5 hour. Finally the dried particles with 8%-Cu (mass fraction to adsorbent) was calcined at a temperature of 400°C for 8 hour. Analysis of the pore characteristic i.e. specific surface area, pore volume and average pore diameter were conducted for fresh and regenerated adsorbent using BET method (Nova 3200eQuantachrome, USA). Analysis on the crystal structures determined byXRD

(Bruker D8 Advance, Germany) was also applied to the active and saturated adsorbent.

2.2 SO_2 Adsorption and Regeneration of Saturated AdsorbentCuO/γ-Al_2O_3

Experiment on adsorption of SO_2on adsorbent CuO/γ-Al_2O_3wereconducted at a temperature of 400°C. The gas model composed of 18500 ppmvSO_2 in air. The initial weight of the adsorbent wasabout 1.0 gram. Regeneration of the saturated adsorbent CuO/γ-Al_2O_3were carried out at various temperatures of 500, 600 or 700°C with air as carrier gas. Both of the adsorption and regeneration experiments were carried out with gas flowratesin the range of 1.4 – 1.8 mL/sec, for 60 minutes. The extent of desorption of saturated adsorbentCuO/γ-Al_2O_3were measured from the different weight of the adsorbent between the beginning and the end of the adsorption, and those of the regeneration process. The extents of desorption were measured from the concentration of SO_3 in the gas leaving the desorption. The experimental set up is presented on Figure 1.



1. Mixed tank
2. Manometer
3. Adsorbent
4. Furnace
5. Temperature controller
6. Bubble soap meter
7. Compressor

Fig. 1. Experimental set up

3. Results and Discussions

3.1 Characteristics ofFresh and Regenerated AdsorbentCuO/γ-Al_2O_3

In general, sintering of pore may happen on pore during adsorption-regeneration process. The pore properties data of the fresh, saturated (sulphated) adsorbent and regenerated adsorbentCuO/γ-Al_2O_3, are summarized and compared in Table 1. The specific surface area of adsorbentCuO/γ-Al_2O_3afterregenerationat temperaturesof 500, 600or 700°Cdecreasedcompared to the freshadsorbent. This might be due to an incomplete decomposition of the saturated adsorbent, leaving some un-decomposed $CuSO_4$.

Even more, result of regeneration of the saturatedadsorbent CuO/γ-Al_2O_3at temperature of700°C, the surface area and averagepore diameter ofthe adsorbentdecrease drastically whichindicated a change of the adsorbent structure. This wasin accordance with thatreportedbyYooetal.[8]. After ten times adsorption-regeneration cycles, thephysicalproperties of the adsorbent changedsignificantly especially for a regeneration temperature of 700°C.

The XRD pattern of the saturated adsorbent and after the adsorption-regeneration cycles as shown in Figure 2. There were no detectable XRD characteristic peaks of $Al_2(SO_4)_3$ (25.4) in a regenerated adsorbent after ten times adsorption-regeneration cycles for regeneration temperatures both at of 600 and 700°C. The X-ray diffraction peaks of the tenth adsorption-regeneration cycle at regeneration temperature of 600°C are quite similar to those of regeneration temperature of 700°C.

Table 1.Comparison adsorbent pore properties of our experiment toliterature data

Adsorbent condition	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	Adsorption-regenerasi cycles	Ref.
Fresh	196.1	0.41	83.2	-	
	186.0	0.39	84.0	-	8
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 500°C	128.1	0.30	93.2	2	
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 600°C	139.5	0.37	107.0	2	
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 700°C	128.1	0.39	122.4	2	
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 500°C	42.9	0.13	116.9	10	
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 600°C	114.1	0.39	135.2	10	
Adsorption at temp. 400°C, regeneration with thermal decomposition at temp. 700°C	76.2	0.41	215.1	10	
Adsorption at temp. 500°C	76.0	0.16	84.0	-	8
Adsorption at temp. 500°and regeneration with 5%H_2+ 95% N_2at temp. 350°C	122	0.23	76.0	-	8
Adsorption at temp. 500°C and regeneration with 5%H_2 + 95% N_2 at temp. 500°C	185	0.35	73.0	-	8
Adsorption at temp. 500°C, regeneration with thermal decomposition at temp. 800°C	111	0.33	120.0	-	8

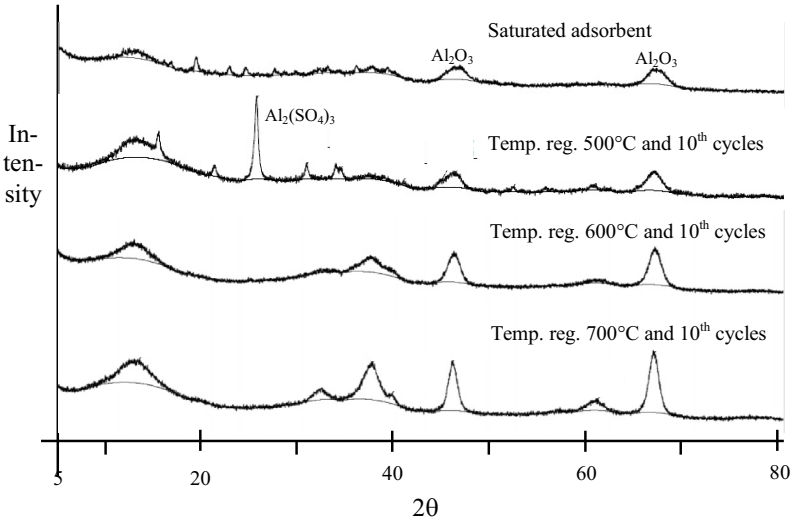


Fig. 2.XRD pattern of adsorbent CuO/γ-Al_2O_3

3.2 Extent of Regeneration AdsorbentCuO/γ-Al_2O_3

Experiments on regeneration or desorption of SO_3 from $CuSO_4$were studied using saturated adsorbentsCuO/γ-Al_2O_3obtained from the similar adsorption conditions. The regeneration were conducted at different regenerationtemperaturesof 500, 600and700°C,and the desorptions of SO_3 as product of $CuSO_4$ decomposition were measured for every successive regeneration. Regeneration at 600°C clearly gave an a highest SO_3 desorption compared to those from 500°C and 700°C (see Figure 3). For regeneration at 500°C, the decomposition of $CuSO_4$ probably did not completed yet and some SO_3 reacted with Al_2O_3 (see the above reaction equation-3 and Figure 2). While for regeneration at 700°C, maybe more caused by the sintering of the alumina support of adsorbent so decrease ability adsorbentCuO/γ-$Al_2O_3$to adsorpSO_2.

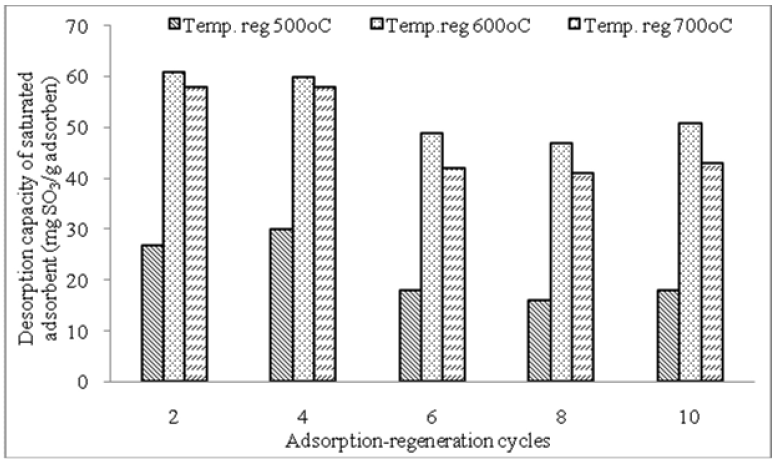


Fig.3.Desorption capacity of saturated adsorbent$CuO/\gamma\text{-}Al_2O_3$

Up to four times, the SO_3 emission from regeneration of saturated adsorbent appeared to be similar (see Fig. 3). But it clearly dropped for the successive sixth and eighth cycles, and then it seemed constant for the tenth cycle. Assuming that the adsorption conditions were quite similar from cycle to the next one, the decrease in the extents of desorption was presumably due to the change in solid characteristics of adsorbent during adsorption and desorption. After the fourth cycle, the characteristics of adsorbent tended to constant.

4. Conclusions

Adsorbent $CuO/\gamma\text{-}Al_2O_3$prepared using the dry impregnation method was tested already for adsorption-desorption up to ten cycles, resulted an acceptable change in its solid characteristic and activity. This experimental study revealed that the regeneration of saturated adsorbent should better be carried out at a temperature of about 600°C.

Acknowledgements

This study is a part of Doctoral Research in Chemical Engineering Doctoral Program FTI-ITB. This study is supported by PT. PupukSriwidjaja Palembang for doctorate program scholarship, as well as research and development of regenerable adsorbent.

References

1. Yuono, Bahrin D, Susanto H. Preparation and Characterization of $CuO/\gamma\text{-}Al_2O_3$ for Adsorption of SO_2 in Flue Gas. *Modern Applied Science* 2015; 9(7): 107-113.
2. Centi G, Passarini N, Perathoner S, Riva A. Combined $DeSO_x/DeNO_x$ Reaction on a Copper on Alumina Sorbent-Catalyst. 1. Mechanism of SO_2 Oxidation-Adsorption. *Industrial and Engineering Chemistry Research* 1992;31: 1947-1955.
3. McCrea DH, Forney AJ, Myers JG. Recovery of Sulfur from Flue Gases Using a Copper Oxide Absorbent.*Journal of the Air Pollution Control Association* 1970; 20 (12): 819-824.
4. Macken C, Hodnett BK, Paparatto G. Testing of the CuO/Al_2O_3 Catalyst-Sorbent in Extended Operation for the Simultaneous Removal of NO*x* and SO_2 from Flue Gases. *Industrial and Engineering Chemistry Research* 2000;39: 3868-3874.
5. Mathieu Y, Tzanis L, Soulard M, Patarin J, Vierling M, Moliere M. Adsorption of SO_x by Oxide Materials: A Review. *Fuel Processing Technology* 2013; 114: 81-100.
6. Xie G, Liu Z, Zhu Z, Liu Q, Ma J. Reductive Regeneration of SufatedCuO/Al_2O_3 Catalyst-Sorbent in Ammonia. *Applied Catalysis B: Environmental* 2003; 45: 213-221.
7. Yoo KS, Kim SD, Park SB. Sulfation of Al_2O_3in Flue Gas Desulfurization by $CuO/\gamma\text{-}Al_2O_3$ Sorbent. *Industrial and Engineering Chemistry Research* 1994; 33: 1786-1791.
8. Yoo KS, Jeon SM, Kim SD, Park SB. Regeneration of Sulfated Alumina Support in $CuO/\gamma\text{-}Al_2O_3$ Sorbent by Hydrogen. *Industrial and Engineering Chemistry Research* 1996; 35: 1543-1549.
9. Ingraham TR. Thermodynamics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate. *Trans. Met. Soc. AIME* 1965; 233: 359-363.